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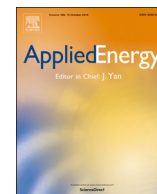To cite this publication, please use the final published version (if applicable).
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On the sustainability of CO_2 storage through CO_2 – Enhanced oil recovery

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HIGHLIGHTS

- The net storage efficiency of carbon capture projects is maximally 6–56%.
- The CO_2 capture and storage process re-emits 0.43–0.94 kg of CO_2 per kg of CO_2 stored.
- Exergy recovery factor of CO_2 enhanced oil recovery depends on CO_2 utilization factor.
- 30–50% of fossil fuel energy is required to capture released CO_2 from its combustion.

ARTICLE INFO

ABSTRACT

This work uses pilot examples of CO_2 enhanced oil recovery to analyze whether and under which circumstances it is exergetically favorable to sequester CO_2 through enhanced oil recovery. We find that the net storage efficiency (ratio between the stored and captured CO_2) of the carbon capture and storage (CCS)-only projects is maximally 6–56% depending on the fuel used in the power plants. With the current state of technology, the CCS process will re-emit a minimum of 0.43–0.94 kg of CO_2 per kg of CO_2 stored. From thermodynamics point of view, CO_2 enhanced oil recovery (EOR) with CCS option is not sustainable, i.e., during the life cycle of the process more energy is consumed than the energy produced from oil. For the CCS to be efficient in reducing CO_2 levels (1) the exergetic cost of CO_2 separation from flue gas should be reduced, and/or (2) the capture process should not lead to additional carbon emission. Furthermore, we find that the exergy recovery factor of CO_2-EOR depends on the CO_2 utilization factor, which is currently in the low range of 2–4 bbl/tCO$_2$ based on the field data. Exergetically, CO_2 EOR with storage option produces 30–40% less exergy compared to conventional CO_2 enhanced oil recovery projects with CO_2 supplied from natural sources; however, this leads to storage of > 400 kg of extra CO_2 per barrel of oil produced.

1. Introduction

It is currently perceived that the elevated concentration of carbon dioxide (CO_2) in the atmosphere (caused by anthropogenic or human activities) is a major contributor to global temperature rise or climate change. Despite major investments in renewable energy, with (ever) increasing global energy demand, the energy supply will largely originate from fossil fuels in the next few decades [1,2], the burning of which emits more than 25Gt of CO_2 every year [3]. To avoid or at least mitigate long-term climate changes, it is therefore prudent to consider measures to reduce CO_2 emissions into the atmosphere. CO_2 *c*apture and its subsequent *s*torage (CCS) in subsurface formations is a means of mitigating greenhouse-gas effects [4]. However, with the current state of technology CCS appears to be costly, which necessitates utilizing CO_2 to cover part of the CCS cost (so-called CCUS or carbon capture, utilization, and storage).

CO_2 enhanced oil recovery (EOR) is a mature technology that has been successfully applied to extract oil from oil reservoirs [5,6]. CO_2 has excellent dissolution properties and above a relatively small pressure (called the minimum-miscibility pressure, MMP) becomes miscible with the in-situ oil and *drags* the oil out of pores through several mechanisms such as interfacial-tension reduction, viscosity reduction and oil swelling. This combined with the availability of the infra-structure and facilities in place, and the structural integrity of the oil reservoirs in containing fluids over very long times provides an opportunity to use CO_2 and store it permanently underground, because the produced hydrocarbons can compensate for part of the CCS cost and reduce the net emission of CO_2 [7,8]. Geographically, depleted oil and gas reservoirs

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are spread all over globe [9]. However, it is doubtful that society will easily comply with the idea of the CO_2 storage in reservoirs that are under or close to residential areas. This implies that CO_2 must be transported to remote (far from CO_2 source) fields, which puts an additional cost on the CCS projects. In addition to economic incentives and increased oil production, the oil industry can benefit from carbon-tax and other socioeconomic incentives by implementing CCS through EOR.

As of 2014, there were more than 136 active CO_2 EOR projects in the US injecting more than three billion standard cubic feet (0.156Mt) of CO_2 [10–12], which is a tiny fraction with respect to the anthropogenic carbon dioxide emissions. However, a large fraction of the injected CO_2 comes from natural sources [12], which cannot contribute to reductions in anthropogenic CO_2 emissions into the atmosphere. The use of natural sources is mainly caused by the large cost of capturing CO_2 from fossil-fuel-fired power plants [13].

Several researchers have analyzed the entire life cycle of the CO_2-EOR projects and, depending on the selected cycle boundary, have estimated the amount of CO_2 emitted from these projects [14,15]. The most important parameter in evaluating the life-cycle of CO_2-EOR is the CO_2 utilization factor (mass or volume of CO_2 required to produce one incremental barrel of oil, (kg CO_2/bbl oil or Mscf CO_2/bbl oil) [16,17]. These studies typically assume an average CO_2 utilization factor and calculate the associated CO_2 footprint of the different (upstream and downstream) stages of CO_2-EOR [18,19]. As a result, these numbers become an average number over the lifetime of the projects and fail to consider that the CO_2 utilization factor will decrease with time and that it depends on the geological heterogeneity of the oil fields. Indeed, as time passes less oil is extracted per volume of CO_2 injected. Also, the amount of recovered oil decreases significantly as the reservoir heterogeneity (mainly spatial variations of the permeability field) increases. Nevertheless, these analyses confirm that the incremental oil produced from CO_2 EOR is a lower-carbon fuel [14]. The CO_2 capture rate and net utilization can be optimized to further decrease the carbon intensity of CO_2-EOR oil. Kwak and Jim [20] performed an economic evaluation of CO_2 EOR with consideration of CO_2 supply from external CO_2 sources. It was concluded the introduction of economic incentives can be a key design parameter for the economics of CO_2 EOR. This contradicts with the findings of Wang et al. [21] that sequestration is insensitive to the CO_2 subsidy at the level of individual projects. Also, oil price and surface and subsurface factors contributing to extra oil gain play important roles on the economics of CO_2 EOR development [22]. Jiang et al. [23] quantified the CO_2 emissions from different components of CCS-EOR system. According to these calculations petroleum combustion and the EOR process release about 67–71% and 14–19% of the total emissions, respectively. Only 5% of the total emission was attributed to the CO_2 capture part. However, the authors did not include the CO_2 arising from the capture process itself.

To the best of our knowledge, majority of the research papers dealing with the life-cycle assessment of CO_2 EOR, have focused on the technical and economic feasibility of the process. However, apart from the cost of the capture and compression, the high energy intensity of the CCS processes triggers the question whether CO_2 storage through EOR is thermodynamically sustainable. Also, it is important to realize that during capture of the CO_2 from power plants additional CO_2 is released, which should be captured if the process meant to be carbon-neutral. This can further question the practicality of the CCS process, especially when the source of the energy is coal. Therefore, the main objective of this paper is to establish a method for the analysis of CO_2 storage through EOR from an exergy-balance perspective [24]. Exergy is defined as the maximum work that can be obtained from an energy stream when it is brought to equilibrium with the environment or its surroundings [25]. The environment is assumed to be in a dead state, which means that it has no potential of creating useful work. Unlike energy, which is conserved through the first law of thermodynamics, exergy is not conserved and can be destroyed because of irreversibilities

and generation of entropy (second law of thermodynamics) [26].

Recently, we have established a workflow to perform an exergy balance (including the exergy destruction terms) for hydrocarbon-production systems. The workflow can be used to improve system's efficiency and/or reduce their carbon footprint [27,28]. These calculations introduce the concept of the exergy-zero recovery factor, which is the maximum fraction of oil in place that can be produced (before the exergy input for recovery exceeds the exergy of the produced hydrocarbon) with a minimum energy waste [27]. Beyond this recovery factor, the exergy gain from reservoirs is less than the invested exergy. The outcome of such an analysis can be used to optimize the energy systems. Moreover, the exergy recovery factor is a measure of sustainability of the hydrocarbon-production systems, which determines the fraction of energy consumed during the process [29].

Our objective is to perform an exergy analysis to assess whether and under which circumstances it is exergetically efficient to store CO_2 through EOR. The concept of exergy-zero time allows us to identify the exergetic break-even point for CO_2-EOR. We will use pilot examples of CO_2-EOR [30] in combination with the modified Koval [31,32] method to generate an estimate of the expected oil production history. We will then identify the main exergy streams that must be considered for CO_2 storage through EOR. This allows us to estimate the exergy recovery factor [13,27] of these processes and therefore identify the main parameters contributing to a positive exergy recovery factor. Moreover, we show that the exergy analysis can identify the bottlenecks, i.e., energy-intensive stages in the overall process, and quantify the scope of possible improvements and optimization of the processes.

2. System definition

Fig. 1 depicts a simple schematic of the system considered in this study. It includes the exergy analysis of the main stages of a CCS project that aims at using CO_2 to extract more oil from an already-producing oil field. The CO_2 source is obtained from power plants powered by fossil fuels. The oil field is assumed to be above its bubble-point pressure, i.e., there is no free gas in the reservoir. However, gas is dissolved in the oil, and its amount can be quantified through the value of the producing gas-oil ratio (GOR) at surface conditions. It is also assumed that the oil field has been already flooded by water, and therefore, CO_2 is injected as a tertiary recovery method. CO_2 is captured from its source (e.g. a power plant), compressed to an initial pressure, and then transported to the oil field. On the field site, the transported CO_2 is re-compressed and then injected into the reservoir. Often, the low viscosity and density of the injected CO_2 result in bypassing of much of the oil in place (OIP). A common practice is to inject alternating slugs of water and CO_2 to mitigate these shortcomings (referred to as WAG or water-alternating-gas scheme in the literature, see Fig. 2). Consequently, we consider water, its treatment, and pumping in our analysis. Usually, water sources are near the field and therefore we neglect water transport in our analysis. However, the water requires further treatment to meet the specifications imposed by the reservoir properties (mainly permeability to avoid pore plugging) and surface facilities and material. Injection of CO_2 and water leads to production of more oil. However, some of the injected fluids will also be produced. The produced fluids are separated at the surface in a separator, and the produced water is transferred to water-treatment facilities for re-injection.

The oil is pumped to a refinery for further processing, after which the final oil product (fuel) is obtained. The produced gas contains both CO_2 and the hydrocarbon gases released from oil. The produced CO_2 is normally re-injected into the reservoir. It is assumed that 50% of the injected CO_2 is retained in the reservoir and therefore there is always need for fresh CO_2 from the source, in accordance with the field applications of CO_2-EOR [30]. The hydrocarbon gas (considered to be methane, CH_4) can either be re-injected with the CO_2 or is used either onsite or offsite. The addition of CH_4 can increase the minimum-miscibility pressure (MMP) and reduce the oil production if CO_2 is meant to
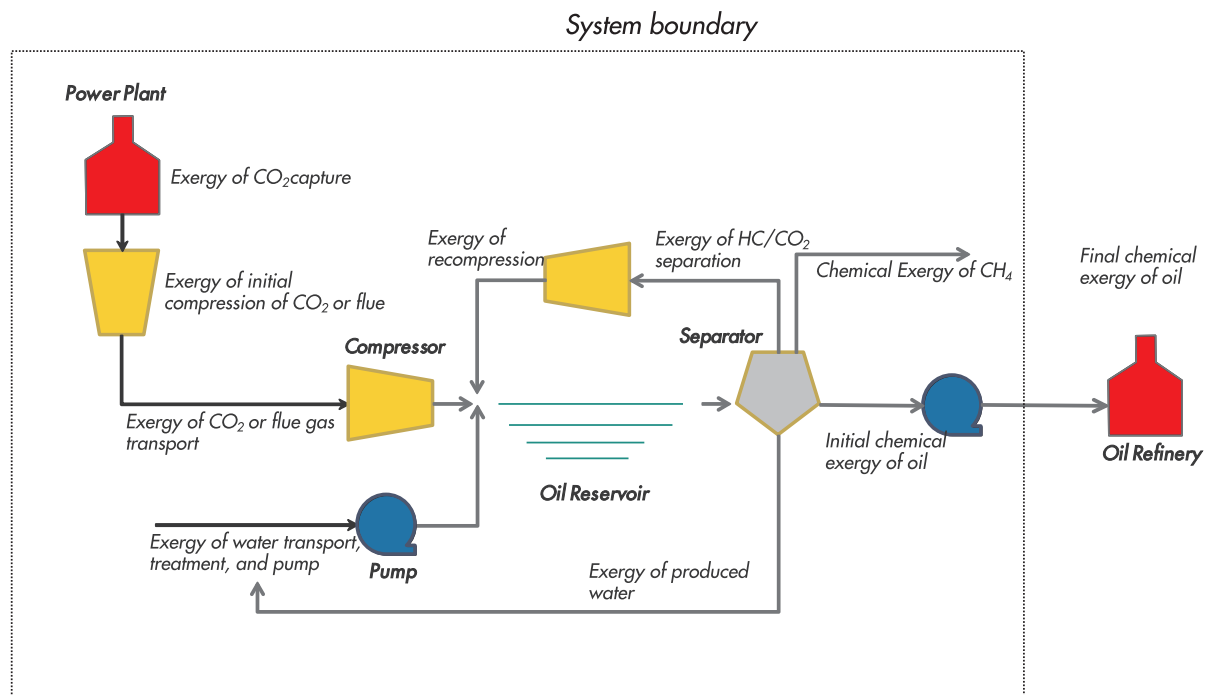
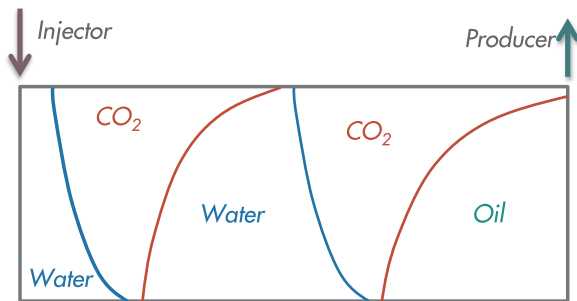Fig. 1. System definition: CO_2 EOR with the CCS option.

Fig. 2. Simple schematic of a CO_2 WAG process: CO_2 and water slug are injected alternately. The regions denoted by CO_2, water, and oil denote the regions where fractional-flow of the corresponding phase is the largest, i.e., in all three regions three-phase flow exists.

be injected under miscible conditions. In the base case (Scenario 1), we assume that only CO_2 is recycled and returned to the reservoir.

3. Exergy analysis

In this section, we describe the exergy streams and material relevant for the CO_2 storage through CO_2 EOR. The general concept and methodology are explained in Appendix A. To perform the exergy analysis, the exergy of the work and material streams should be first calculated for the defined system in Fig. 1.

3.1. Exergy streams

The main exergy streams of a CO_2 EOR project are shown in Fig. 1. In this section, we expand each stream and calculate its corresponding exergy. The streams can be broken down into *material* and *work* streams.

3.1.1. Material streams

The chemical exergy of crude oil depends on its composition and it is generally assumed to be its lower heating value (LHV). The following equation correlates the chemical exergy of oil to its specific gravity (SG)

[33]

$$LHV \left[\frac{MJ}{kg} \right] = 55.5 - 14.4 SG$$

(1)

Assuming *SG = 0.70,* the exergy of the crude oil is 45.5 MJ/kg.

We assume that the gas released from oil is methane. The chemical exergy of CH_4 is $Ex^{ch}_{CH_4} = 831.65$ kJ/mol or 51.98 MJ/kg [34,35]. When CO_2 is injected into the reservoir the produced gas will contain CO_2. However, the chemical exergies of CO_2 and the produced water are neglected because their chemical exergy has a negligible impact on the final results; their exergy values are at least four factors of ten smaller than that for oil.

3.1.2. Work streams

We performed the calculation of the thermodynamic properties of the streams, unless stated otherwise, using the CoolProp freeware [36]. CoolProp calculates the thermodynamic and transport properties of industrially-important fluids and their mixtures. It uses a multi-parameter Helmholtz-energy-explicit-type formulation for thermodynamic properties and a variety of methods, including the extended corresponding states for transport properties. CoolProp is available at www.coolprop.org for multiple platforms and computational tools, including Excel. The exergy of work streams identified in Fig. 1 are provided in the following.

3.1.2.1. Exergy of CO_2 capture.
The CO_2 capture methods (from mixtures containing carbon dioxide, methane, nitrogen) consume large amounts of energy [13,37–41]. For this study it is assumed that $Ex^{pr}_{capture} = 4000$ kJ/kg CO_2, which is the average exergy value required for separating CO_2 from flue gas in the chemical absorption of CO_2 using an aqueous solution of MEA (mono-ethanol-amine), today's predominant carbon-capture technology. Capture costs can be reduced by using membrane technology, but this is not widely used, being insufficiently mature.

3.1.2.2. Exergy of CO_2 transport, compression and injection.
To calculate exergy of CO_2 transport, compression, and injection we followed the procedure explained by ref. [13]. We assume that CO_2 is transported
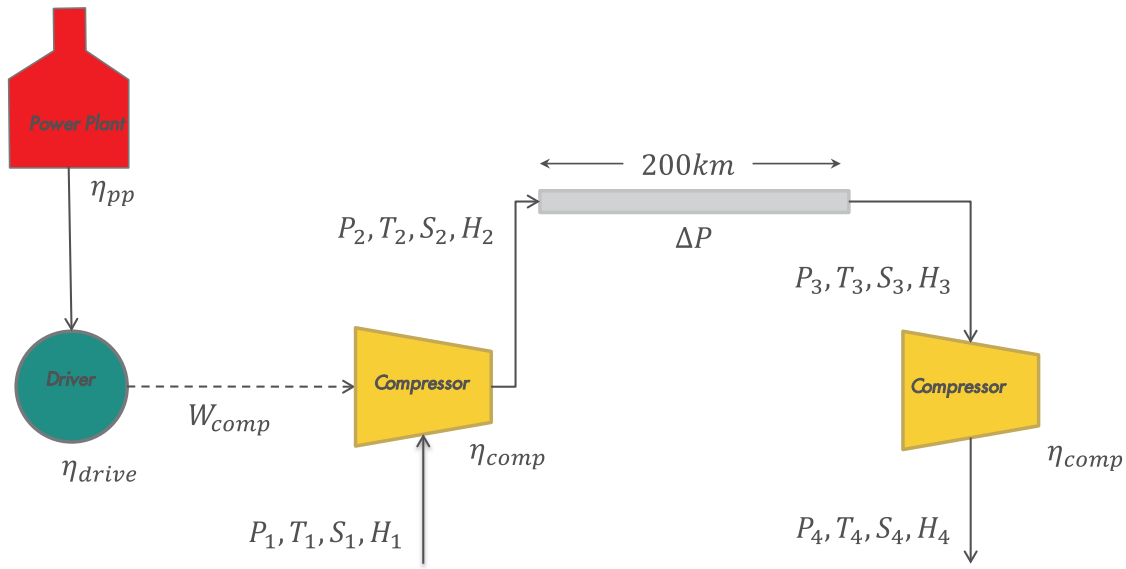
Fig. 3. Transport of CO_2 by pipeline and reservoir injection.

through a 200 km long pipeline system from a source power plant to the sink oil reservoir. The transport and injection layout system is shown in Fig. 3.

The captured CO_2 enters the transport compressor at a known temperature T_1 and pressure P_1 and leaves it at the elevated temperature T_2 and pressure P_2. Compression is an isentropic (adiabatic) process or the entropy of the streams remain constant. Similarly, the CO_2 enters the injection compressor at a temperature T_3 and pressure P_3 and exits at the desired pressure P_4.

The minimum exergy requirements of the two adiabatic compression stages are the enthalpy differences between the input and output streams at constant entropy, which we call the theoretical exergy of compression. For the practical exergy value, i.e., a state of the art compressor, the efficiencies of the compressor, electrical driver and the power plant should also be considered. Thus,

$$Ex_{CO_2}^{pr,trans} = \frac{Ex_{CO_2}^{th,comp1}}{\eta_{comp}\eta_{driver}\eta_{pp}} = \frac{H_2(S_1(T_1,P_1),P_2) - H_1(S_1(T_1,P_1),P_1)}{\eta_{comp}\eta_{driver}\eta_{pp}} \quad (2)$$

and

$$Ex_{CO_2}^{pr,inj} = \frac{Ex_{CO_2}^{th,comp2}}{\eta_{comp}\eta_{driver}\eta_{pp}} = \frac{H_4(S_1(T_1,P_1),P_4) - H_3(S_1(T_1,P_1),P_3)}{\eta_{comp}\eta_{driver}\eta_{pp}} \quad (3)$$

The total practical exergy of compression is the sum of the exergy of compression for transport and for injection, i.e.,

$$Ex_{CO_2}^{pr,comp} = Ex_{CO_2}^{pr,trans} + Ex_{CO_2}^{pr,inj} \quad (4)$$

The following steps are taken to calculate the exergy of CO_2 transport and injection

- Isentropic compression is assumed for all streams, i.e., $S_2 = S_1$ and $S_4 = S_3$.
- For stream 1, the values of enthalpy and entropy are calculated using CoolProp.
- The pressure drop in the pipeline is calculated using the Panhandle equation [42]; The pipe diameter is calculated by assuming a maximum allowable velocity for the gas stream (here a 20-inch diameter pipeline). All the transport properties are calculated with CoolProp.
- We assume a pressure for the gas stream at the outlet of the transport pipeline, e.g., $P_3 = 80$ bar. The pressure of stream 2 (P_2) is then $P_2 = P_3 + \Delta P_{pipe}$.

- For the calculation of the theoretical compression exergy, we consider a multistage compressor with inter-stage cooling where the pressure of the output stream from each stage is calculated using pressure ratio of typical compression processes ($P_2/P_1 = 3.0 – 4.5$ for a centrifugal compressor [13]). The input temperature to each stage is T_1.
- The enthalpy of the output streams from each compression stage is calculated for the known pressure and entropy.
- The isentropic compression work for each case is the difference in enthalpy ΔH between the input and output streams.
- We use a typical current values for the compressor efficiencies and the power generating efficiencies, i.e., $\eta_{pp} = 0.40$, $\eta_{drive} = 0.90$, and $\eta_{comp} = 0.70$.

The injection pressure P_4, as well as the CO_2 injection rate are taken to be 280 bar and $\sim 30{,}000$ m^3/d (at reservoir conditions). The results of the compression exergy requirements in the transport and injection compressors are shown in Table 1.

3.1.2.3. Exergy of oil transport to the refinery. For the calculation of the exergy of oil transport, an average flow rate of 2.88 kg/s, diameter of pipeline 3 in., average flow speed of 0.8 m/s, an initial pressure of 200 bars, and a transporting distance of 200 km to the refinery were assumed.

Using the Darcy–Weisbach equation for fluid pressure drop in pipeline transportation, and taking into account that at the end of the pipeline the crude oil need only be at a slightly higher pressure than atmospheric, a pressure loss of $\Delta P = 196$ bar is calculated. The theoretical pumping exergy required for the pumps to transport the crude

Table 1
Compression exergy in the transport and injection of CO_2.

	Transport	Injection	Unit
P_{in}	1	80	bar
P_{out}	80	280	bar
Max pressure ratio	3	3	
η_{comp}	0.70	0.70	
η_{driver}	0.90	0.90	
$\eta_{powerplant}$	0.40	0.40	
$Ex_{CO_2}^{th,comp}$	354	59	kJ/kg CO_2
$Ex_{CO_2}^{pr,comp}$	1405	235	kJ/kg CO_2

oil under the above conditions is given as an approximation by:

$$Ex_{oil}^{th,trans} = Ex_{pump} = \dot{Q}\Delta P \tag{5}$$

where $\dot{Q}\left[\frac{m^3}{s}\right]$ stands for the flow rate of the crude oil through the pipeline and ΔP [Pa] is the pressure drop in the pipeline. The practical pumping exergy is calculated by including the mechanical efficiency of the pump (80%), and efficiency of the electrical driver (90%), and the power plant (45%), i.e.,

$$Ex_{oil}^{pr,trans} = \frac{Ex_{oil}^{th,trans}}{\eta_{pump}\eta_{driver}\eta_{pp}} = \frac{\dot{Q}\Delta P}{\eta_{pump}\eta_{driver}\eta_{pp}} \tag{6}$$

This amounts to a value of $Ex_{oil}^{pr,trans} = 2.6$ kJ/s, which in turn, normalized over the lifetime of the project and the total amount of oil transported amounts to 75.4 kJ/kg of oil transported.

3.1.2.4. Exergy of gas (CO$_2$/HC) separation.

The separation of the gases from the liquid oil is assumed to take place in a gravity separator vessel; therefore there is no need to spend exergy in this step. The subsequent separation of the CO_2 from the hydrocarbons in the gaseous mixture is assumed to $Ex_{CO_2}^{pr,sep} = 2500$ kJ/kg of CO_2 captured.

3.2. Exergy recovery factor

We define the exergy recovery factor, Ex_{RF}, as the ratio of the produced exergy corrected for material and process exergy requirements for its extraction and to the gross exergy of the source, i.e.,

$$Ex_{RF} = \frac{Ex_{gained} - Ex_{invested}}{Ex_{fuel}} \tag{7}$$

Ex_{gained} is the exergy of the final product (within the selected boundary), $Ex_{invested}$ is the amount of exergy invested to produce hydrocarbons, and Ex_{fuel} is the amount of exergy stored in the hydrocarbon reservoir [27]. For the case considered here, i.e. a CO_2 EOR project with CCS option, Eq. (7) becomes

$$Ex_{RF} = \frac{(Ex_{oil}^{ch} + Ex_{CH_4}^{ch}) - (Ex_{CO_2}^{capture} + Ex_{CO_2}^{comp} + Ex_{CH_4}^{comp} + Ex_{water}^{treat} + Ex_{CO_2}^{sep} + Ex_{oil}^{trans})}{Ex_{oil}^{ch} + Ex_{CH_4}^{ch}} \tag{8}$$

4. Calculation of oil recovery

We follow the procedure developed by Walsh and Lake [8] to calculate oil recovery when CO_2 is injected alternately with water to displace oil in a 1-D porous medium. For simplicity, we ignore CO_2 dissolution in oil and water. This method requires construction of water-oil and water-solvent fractional-flow functions. The fractional-flow function of phase i displacing phase j is defined as

$$f_{ij} = \frac{1}{1 + \frac{1}{M_{ij}}} \tag{9}$$

where M_{ij} is the mobility ratio function between the displacing phase i and displaced phases j and is defined as

$$M_{ij} = \frac{k_{r_i}}{k_{r_j}}\frac{\mu_j}{\mu_i} \tag{10}$$

k_{rk} the relative permeability of phase k, is calculated using a Corey-type model [6]. Fig. 4 shows examples of the fractional-flow curves calculated for the water-oil and the water-solvent pairs. Point J on the water-solvent fractional-flow curve is determined using volumetric ratio of water and CO_2 rates (WAG ratio), W_R:

$$f_{wJ} = \frac{W_R}{1 + W_R} \tag{11}$$

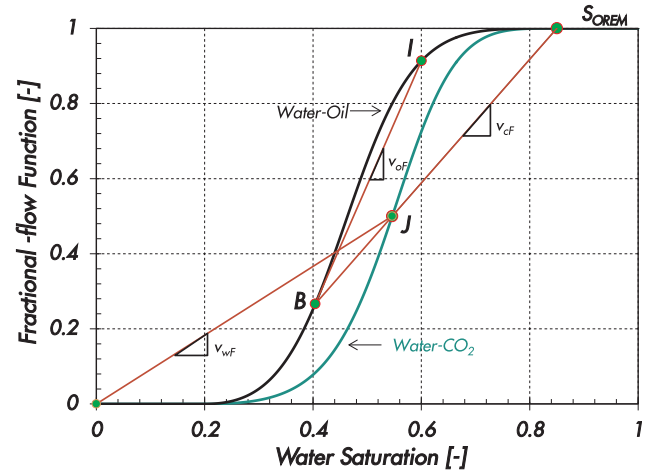The specific velocity of CO_2 front, v_{cF}, is determined from the slope

Fig. 4. Graphical representation of solution of oil displacement by miscible CO_2 using WAG scheme. S_{OREM} stands for remaining oil saturation.

of the line connecting point $(1 - S_{OREM}, 1)$ to point J (injected composition/saturation) the extension of which intersects the water-oil fractional-flow curve at point B. The velocity of the oil bank, v_{oF}, is then the slope of the line connecting point B to point I (initial composition/saturation). The velocity of the water front, v_{wF}, is given by the slope of the line connecting point $(0,0)$ to point J. The optimal WAG ratio, in terms of oil recovery, is where point J is chosen such that $v_{cF} = v_{wF}$.

The upscaling of the results obtained from the analytical method is done using the modified Koval's method [31,32]. In this method both the oil-bank and solvent fronts are distorted because of the heterogeneity of the porous medium and/or the adverse mobility ratio and gravity effects. The extent of non-ideality or deviation from the results of the 1-D analytical method is quantified by two Koval factors, K_{oB} for the oil bank and K_S for the solvent bank, which are functions of the Dykstra-Parsons coefficient [43,44]. The main consequences of the non-ideal displacement are (much) earlier breakthrough of the oil and solvent banks, smaller oil cuts, and elongated production times (red curves in Fig. 5).

The production histories of several large-scale applications of CO_2 EOR have been matched to the modified Koval method and their corresponding K_{OB} and K_S values have been obtained. Based on these values, and using the reservoir and fluid properties in Table 2, we created three production histories shown in Fig. 6. It is noticeable that as the reservoir heterogeneity increases, the amount of oil produced by the injected CO_2 decreases. In other words, the CO_2 utilization factor (amount of injected CO_2 per amount of produced oil expressed in Mscf/bbl oil) increases with the increase in the reservoir heterogeneity (Koval factor). The production histories shown in Fig. 6 are a good representation of the large-scale results of 37 CO_2 EOR projects summarized in Ref. [30]. The recovery factors from these projects range between 5 and 25% of the initial oil in place, with an average recovery of about 13% after 3 pore volume of fluid injection (CO_2 and water).

5. Results and discussion

5.1. Exergy of CO_2 capture and storage

In the case of CCS only, CO_2 should be captured and transported to the subsurface formation for underground storage. We assume that the captured CO_2 is compressed to a sufficiently high pressure at the capture site so that no recompression is required in the storage site. Therefore, the *minimum* required exergy to store a unit mass of CO_2 (or specific exergy of the CCS expressed in J/kg) can be calculated from

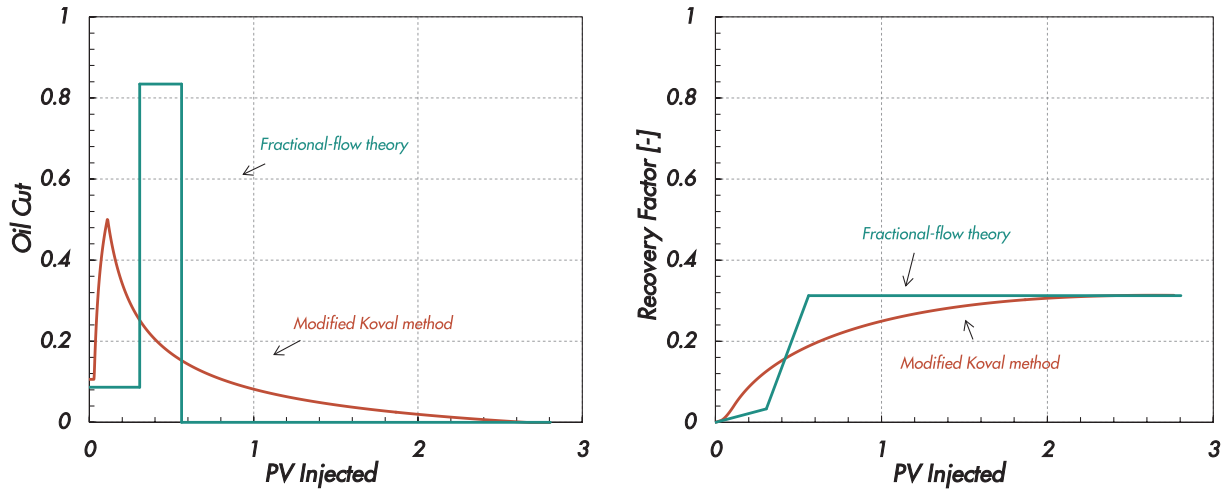$$\dot{ex} = \dot{ex}_{capture} + \dot{ex}_{compression} + \dot{ex}_{transport} \tag{12}$$

Fig. 5. Upscaling of the 1-D analytical results (green curves) using $K_{OB} = 10$ and $K_S = 5$ (red curves).

Table 2
Parameters used to construct the oil recovery histories in Fig. 6.

| Parameter	Value	Description
n_w (n_{ws})	2	Water (water-solvent) Corey exponent
n_o (n_{os})	3.5	Oil (oil-solvent) Corey exponent
k_{rw}^e	0.325	Water end-point relative permeability
k_{ro}^e	0.66	Oil end-point relative permeability
S_{ori}	0.50	Initial oil saturation before CO_2 injection
S_{orw}	0.30	"remaining" oil saturation to water
S_{ors}	0.20	"remaining" oil saturation to CO_2
S_{wc}	0.20	Connate water saturation
μ_S	0.1	CO_2 viscosity (cP)
μ_w	1	Water viscosity (cP)
μ_o	2	Oil viscosity (cP)
WAG ratio	2:1	CO_2:water
Reservoir pore volume	1×10^8 m^3	
Injection rate	0.1 PV/year	
B_o	1.2	
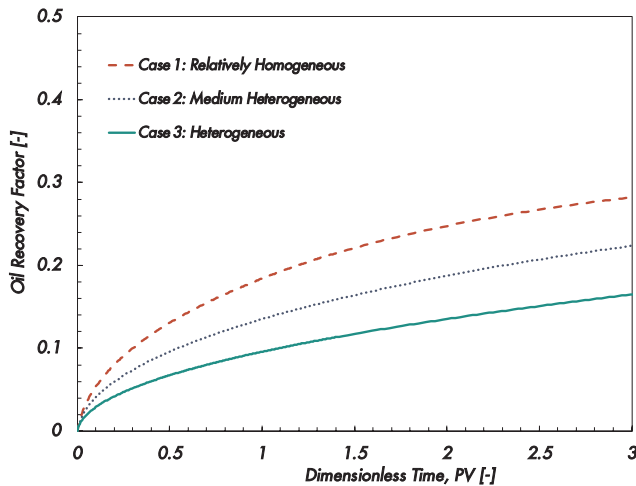
Fig. 6. History of the oil recovery factor (R_F) for the three cases considered in this study. The reservoir heterogeneity reduces the R_F.

For the case considered in this study, the specific exergy of CCS is calculated to be ~ 5.5 MJ/kgCO$_2$ (~ 1.5 kWh/kgCO$_2$). This value does not consider material, wells, or any CO_2 loss during the project, which might occur in practice because of leaks (fugitive emissions), pigging (cleaning and checking pipe line condition), maintenance, etc. To estimate the amount of CO_2 generated during the CCS process, the source of the electricity generation, i.e., the power plant fuel should be known. The fossil fuel CH_α can be natural gas (CH$_4$), oil (CH$_2$), or coal (CH) with estimated heating values of 800 kJ/mol (50 MJ/kg-CH$_4$), 600 kJ/mol (42.85 MJ/kg-CH$_2$)[1], and 500 kJ/mol (38.46 MJ/kg-CH), respectively.

5.1.1. Specific CO_2 emission

Methane: Without considering the CO_2 emitted from mining or extraction processes, burning of methane results in specific CO_2 emission of,

$$\frac{44}{16} \frac{\text{kg } CO_2}{\text{kg } CH_4} \times \frac{1}{50} \frac{\text{kg } CH_4}{\text{MJ}} = 0.055 \frac{\text{kg } CO_2}{\text{MJ} - CH4} \qquad (13)$$

Oil: Similar calculations provide specific CO_2 emission of 0.073 kgCO$_2$/MJ-CH$_2$ (44/14/42.85) for oil.

Coal: in the same way we obtain 0.088 kgCO$_2$/MJ-CH (44/13/38.46) for coal.

Therefore, if CO_2 is stored at the exergetic cost of 5.5 MJ/kg-CO$_2$:

5.1.2. Exergy of multistep CO_2 capture

Methane: (5.5 [MJ-CH$_4$/kg-CO$_2$] $\times$ 0.055 [kg-CO$_2$/MJ-methane]) $\times$ 100 = 30.25% of methane energy must be used for a single storage step. It is also needed to capture and store the carbon dioxide resulting from the energy loss. This means that in the cumulative sense we have to compensate for the exergy loss by producing CH$_4$, and compensate for the loss and thus multiply this number by

$$\Sigma(1 + 0.3025 + (0.3025 \times 0.3025) + \cdots) = 1/(1 - 0.3025)$$
$$= 1.433 \frac{\text{exergy } CH_4 \text{ multiple steps}}{\text{exergy } CH_4 \text{ single step}} \qquad (14)$$

to account for storage of CO_2 when methane is used as the energy source. This implies that 43% of the produced energy will be used for storage in the case of methane combustion, which leads to total actual exergy investment of:

$$1.433 \frac{\text{exergy } CH4 \text{ multiple steps}}{\text{exergy } CH4 \text{ single step}} \frac{\textit{actual } \text{MJ}}{\textit{required } \text{MJ}} \times 5.5 \frac{\text{MJ}}{\text{kg } CO_2}$$
$$= 7.88 \frac{\text{MJ}}{\text{kg } CO_2} \qquad (15)$$

Oil: (5.5 $\times$ 0.073) $\times$ 100 = 40.15% of oil energy must be used for a single storage step. It is also needed to capture and store the carbon

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[1] One bbl = 158.99 L 0.159 m^3. Average density 850 kg/m^3 → 1 bbl 135 kg. This corresponds to 135 kg $\times$ 42.85MJ/kg = 5791 MJ or 1608 kWh.

dioxide resulting from the energy loss. This means that in the cumulative sense we have to multiply this number by

$$\Sigma(1 + 0.4015 + (0.4015 \times 0.4015) + \cdots) = 1/(1 - 0.4015)$$
$$= 1.671 \frac{exergy\ oil\ multiple\ steps}{exergy\ oil\ single\ step} \quad (16)$$

to account for storage of CO_2 when oil is used as the energy source. This implies that 67% of the produced energy will be used for storage in the case of oil combustion, which leads to total actual exergy investment of:

$$1.671 \frac{exergy\ oil\ multiple\ steps}{exergy\ oil\ single\ step} \frac{actual\ MJ}{required\ MJ} \times 5.5 \frac{MJ}{kgCO_2} = 9.19 \frac{MJ}{kgCO_2} \quad (17)$$

Coal $(5.5 \times 0.088) \times 100 = 48.4\%$ of coal energy must be used for a single storage step. It is also needed to capture and store the carbon dioxide resulting from the energy loss. This means that in the cumulative sense we have to multiply this number by

$$\Sigma(1 + 0.484 + (0.484 \times 0.484) + \cdots) = 1/(1 - 0.484)$$
$$= 1.937 \frac{exergy\ coal\ multiple\ steps}{exergy\ coal\ single\ step} \quad (18)$$

to account for storage of CO_2 when coal is used as the energy source. This implies that 93.7% of the produced energy will be used for storage in the case of coal combustion, which leads to total actual storage exergy investment of:

$$1.937 \frac{exergy\ coal\ multiplesteps}{exergycoalsinglestep} \frac{actual\ MJ}{required\ MJ} \times 5.5 \frac{MJ}{kgCO_2}$$
$$= 10.65 \frac{MJ}{kgCO_2} \quad (19)$$

5.1.3. Full-cycle or total CO_2 emission

Methane. The value of 7.88 MJ/kg-CO_2 (see Eq. (15)) is the actual exergy required to store one kilogram of the original or net CO_2 released from a gas-fired power plant (this is referred to carbon-zero or carbon-neutral option). Additionally, for storage of the original CO_2 and the CO_2 generated in the subsequent stages, total CO_2 emission of

$$1.43 \frac{exergy\ CH4\ multiple\ steps}{exergy\ CH4\ single\ step} \times 0.055 \frac{kgCO_2}{MJ - CH_4} = 0.0788 \frac{kgCO_2}{MJ - CH_4} \quad (20)$$

is expected.

Oil: Similarly, for an oil-fired power plant the total specific CO_2 emission will be:

$$1.67 \frac{exergy\ oil\ multiple\ steps}{exergy\ oil\ single\ step} \times 0.073 \frac{kgCO_2}{MJ - CH_2} = 0.122 \frac{kgCO_2}{MJ - CH_2} \quad (21)$$

Coal: Finally, for when coal is combusted in the power plant, the total CO_2 emission will be

$$1.937 \frac{exergy\ coal\ multiple\ steps}{exergy\ coal\ single\ step} \times 0.088 \frac{kgCO_2}{MJ - CH} = 0.17 \frac{kgCO_2}{MJ - CH} \quad (22)$$

In summary, these numbers lead to a minimum additional release of 0.433, 0.671, and 0.937 kg of CO_2 per 1 kg of stored CO_2 for methane, oil, and coal, respectively. Therefore, the maximum net storage efficiency of the CCS projects are on average ~6–56% (100–93.7 via 100–67.1 to 100–43.3) of the captured CO_2 directly released from power plants, assuming a capture efficiency of 100% (which is not practical). With a practical capture efficiency of 90% (referred to as low-carbon option), cumulatively about 11% (1/0.9 = 1.11) of the CO_2 will be emitted directly to the atmosphere and therefore, the net storage efficiency reduces down to (56–11) = 45% for gas, and (33–11) = 22%

Table 3
Summary of the calculations for CCS case only, assuming specific CCS exergy of 5.5 MJ/kg CO_2.

	Gas (CH_4)	Oil (CH_2)	Coal (CH)
Estimated heating value, (MJ/kg)	50	42.85	38.46
Specific CO_2 emission, (kgCO_2/MJ)	0.055	0.073	0.088
Fraction of energy used for CCS or energy penalty of CCS	0.30	0.40	0.48
Actual storage exergy, MJ/kg CO_2	7.88	9.19	10.6
Total CO_2 emission, kgCO_2/MJ-fuel	0.0788	0.122	0.170
Mass CO_2 emitted/mass CO_2 stored, kg/kg	0.433	0.671	0.937
Net CO_2 storage efficiency, % of the stored CO_2 directly released from the power plant (100% capture efficiency)	56	33	6
Net CO_2 storage efficiency, % of the stored CO_2 directly released from the power plant (90% capture efficiency)	45	22	< 0

for oil and negative for coal. Capture of CO_2 from coal power plants will result in net emission of more CO_2 to the atmosphere. Therefore, to reduce the negative impact of CO_2 on climate change through CCS, it is necessary to reduce the exergetic cost of CO_2 capture and/or to use greener (low-carbon) sources of energy during the process. These results are summarized in Table 3.

5.2. Exergy analysis of CO_2 EOR

In the analysis provided in this section, three scenarios were considered for the utilization of the produced gas. In the first scenario (denoted by S1 or Scenario 1), it was assumed that all the produced gas without separation is re-injected back into the reservoir and thus without consuming significant amount of exergy except for that associated with recompression. However, this comes at the cost of losing the exergy gain from the produced methane in Eq. (8). In Scenario 2 (S2), it was assumed that the produced methane is separated from the gas stream and only CO_2 is reinjected into the reservoir. In Scenario 3 (S3), it was assumed that fresh CO_2 is continuously supplied to the project (not a practical scenario).

The calculated exergy-recovery factors (Ex_{RF}) corresponding to the oil-recovery histories (demonstrated in Fig. 6) and considering S1 for the produced gas are shown in Fig. 7. CO_2 is supplied from the captured CO_2 from an oil-fueled power plant. The exergy recovery factor decreases with time, indicating that more exergy is required to produce the oil as project lifetime increases. This is because of the combined effect of the decline in oil production (or exergy gain) and the increase in gas production (or exergy investment). Moreover, it appears from Fig. 7 that the exergy-recovery factor is a strong function of the heterogeneity of the reservoir and, for a given time, its value decreases with an increase in the reservoir heterogeneity. Above a certain time, the exergy recovery factor becomes negative. This time is referred to as exergy-zero time (shown with a red dot in Fig. 7a) is the time above which the exergy required to produce the oil becomes larger than the exergy gained from oil (Farajzadeh, 2019). From the thermodynamic point of view, beyond this time the project is no longer sustainable. At the exergy-zero time, the recovery factor in the field has reached the exergy-zero recovery factor (shown with a red dot in Fig. 7b), whose value increases with decreasing level of the rock heterogeneity.

An interesting feature of the analysis is shown in Fig. 8, where the exergy recovery factors of the three cases are plotted as a function of the (volumetric) gross CO_2 utilization factor, i.e., the gross volume of CO_2 required to produce a unit volume of oil. It appears that the exergy recovery factor is merely a function of the CO_2 utilization factor. As CO_2 utilization factor increases the exergy factor decreases, which is due to the larger quantity of the invested exergy in supplying the injected CO_2. For comparison, the exergy recovery factor of the cases with the natural source of CO_2 and the low-carbon option have also been plotted on the
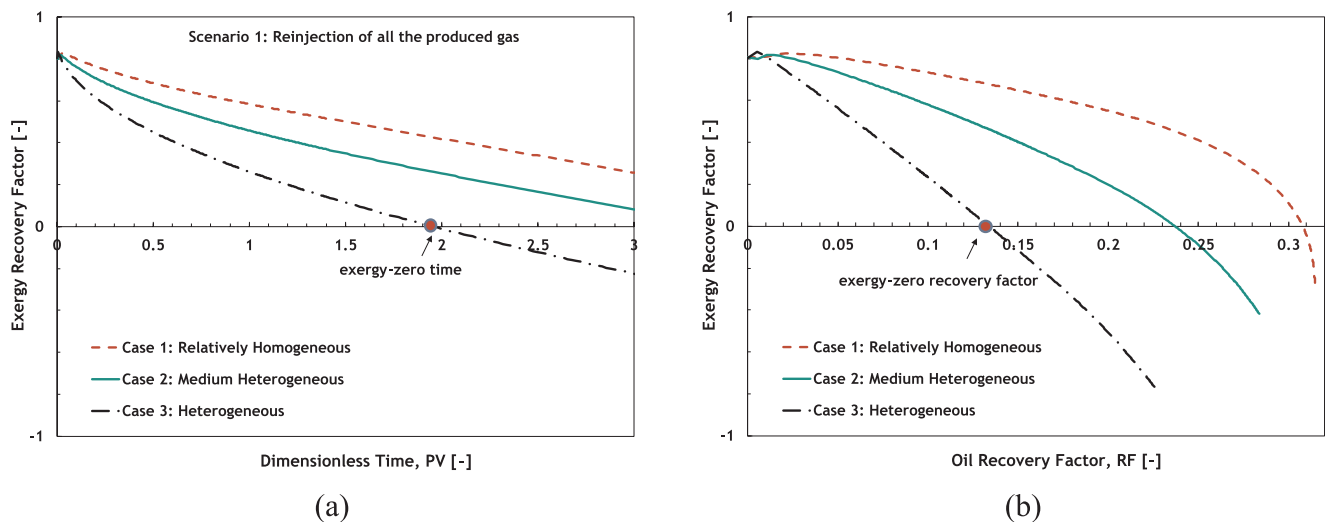
(a)

(b)

Fig. 7. Exergy recovery factor as a function of time (a) and oil recovery factor (b) for the three oil recovery histories presented in Fig. 6. It was assumed that all the produced gas is reinjected back into the reservoir (S1). The CO_2 source is the captured CO_2 from an oil-fueled power plant.
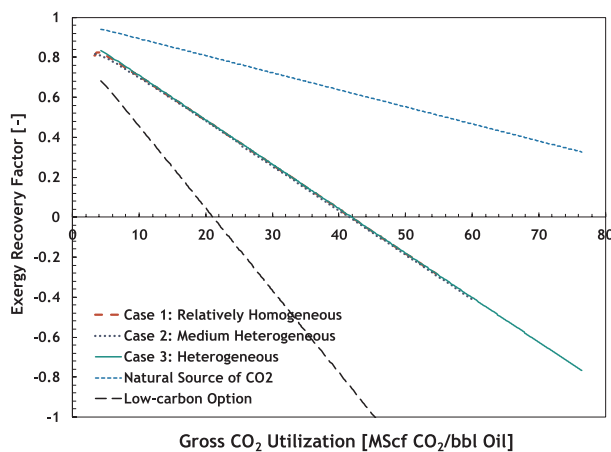

Fig. 8. Exergy recovery factor as a function of gross CO_2 utilization factor for Scenario 1 (all the produced gas is reinjected back into the reservoir). The exergy recovery factor is independent of the reservoir heterogeneity. The dashed blue line considers CO_2 from natural sources (zero capture exergy) and the dashed black line assumes that 90% of the CO_2 generated during the CCUS cycle is captured and stored.

figure. For the case with natural source of CO_2 zero capture exergy has been assumed. For the low-carbon option, capture exergy of 9.19 MJ/kg CO_2 (see Table 3) with a capture efficiency of 90% have been considered. Utilization of the natural sources of CO_2 for extracting oil is a favorable process from exergy point of view; however, it will not be beneficial for negative emission or storage of CO_2. For the low-carbon option, where 90% of the CO_2 arising from the capture, transportation, and compression stages are also captured, the exergy recovery factor is smaller than the other cases. This eventually leads to a smaller exergy-zero gas utilization factor.

The CO_2 utilization factor depends on the petrophysical and thermodynamic properties of the oil-bearing reservoir. For example, highly heterogeneous reservoirs consume more CO_2 compared to the homogeneous ones to produce the same amount of oil. Also, because the surface expansion of CO_2 (expressed as formation volume factor, B_g) depends on the initial pressure of the reservoir, the CO_2 utilization varies with pressure. As a result, in some literature the utilization factor is expressed as the volume of oil per unit mass of injected CO_2 [bbl oil/ kg CO_2]. Fig. 9 shows the exergy recovery factor as functions of mass CO_2 utilization factor (left) and pore volume injected (right). As

expected, the exergy recovery factor for the case with the natural source of CO_2 is larger than the other two cases. Also, with natural source of CO_2, the exergy recovery factor remains positive for all times, i.e., the exergy obtained from the hydrocarbons is always larger than the exergy invested to produce. For the low-carbon option the exergy recovery is smaller compared to the other cases. For example, for CO_2 utilization factor of 2 bbl oil/tonne CO_2, the exergy recovery factor drops from 87% to 41% (see Fig. 9a, green dashed to red dash-dot curve) when the gas source is switched from natural source to the CO_2 captured from power plants. In other words, about 60% of the exergy obtained from oil is consumed for the production of that oil. Furthermore, it appears from the right plot in Fig. 9 that shortly after start of the gas injection (about 0.5 pore volume), the exergy recovery factor becomes negative for the low-carbon option. This means that from thermodynamic point of view, utilization of CO_2 captured from power plants as an EOR agent is not sustainable.

Fig. 10 shows the amount of the emitted CO_2 per barrel of oil as a function of the (net and gross) mass of injected CO_2. An average value of 436 g CO_2/kWhe (oil as the fuel in the power plant) has been assumed in the calculations. This figure also includes the CO_2 released from combustion of the oil, which is calculated to be 422.7 kgCO_2/bbl[2] for the case considered here. Fig. 10 indicates that CO_2 mass utilization factor has a considerable effect on the life-cycle analysis of the CO_2-EOR process, which agrees with the findings of Refs. [14–17]. The analysis of the results of 31 CO_2-EOR projects provides an average net mass CO_2 utilization factor of ~2 bbl oil/tonne CO_2 (with a range of 1.8–4.2 bbl oil/tonne CO_2). The large value of 4.2 bbl oil/tonne CO_2 applies to less than 10% of the published results [30]. Such an optimal result can occur when reservoir conditions are optimal. Optimal conditions are partly the consequence of fixed conditions and partly to conditions such as the mobility ratio that can be manipulated, by injection of foam or other gas thickeners.

It also appears from Fig. 10 that even though the exergy recovery factor of the case with natural source of CO_2 is large, so is its CO_2 footprint (480–550 kgCO_2/bbl for CO_2 utilization factor of 4–2 bbl oil/tonne CO_2). By using the CO_2 captured from power plants, CO_2-EOR process gives an average value of 114 kg CO_2 per barrel of produced oil for CO_2 utilization factor of 2 bbl oil/tonne CO_2. If the CO_2 utilization factor is increased to 4 bbl oil/tonne CO_2 the unit CO_2 emission of CO_2

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[2] One bbl = 5791 MJ or 1608 kWh. With specific CO_2 emission of 0.073 kgCO_2/MJ-CH_2, one bbl of oil produces 5971 MJ × 0.073 kgCO_2/MJ-CH_2 = 422.7 kgCO_2.
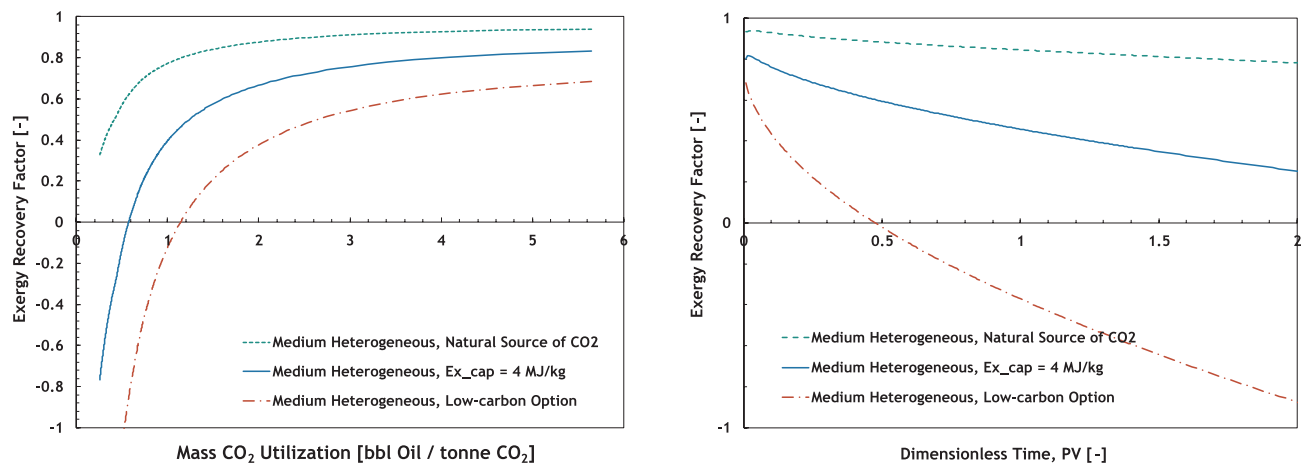
Fig. 9. Exergy recovery factor as function of mass CO_2 utilization (left) and total pore volume injected (right).

EOR reduces to less than 80 $kgCO_2$/bbl. The difference between the two curves with open symbols in Fig. 10 is the amount of CO_2 stored in the CO_2 EOR process, when CO_2 is supplied from an anthropogenic source (or captured). In summary, with CO_2 coming from an anthropogenic source, on average 30–40% less exergy is extracted from oil compared to the case with natural source of CO_2; however, this leads to storage of more than 400 kg of extra carbon dioxide per barrel of oil produced, which can help mitigate the negative impacts of CO_2 on the climate change.

Fig. 11 shows the effect of gas separation on the exergy recovery factor. The oil recovery profile of Case 2 (medium heterogeneous) was used in the calculations. In Scenario 2, it was assumed that methane is separated from the gas stream and only CO_2 is reinjected into the reservoir. In Scenario 3, it was assumed that fresh CO_2 is continuously supplied to the project (not a practical case). Indeed, because gas separation is exergetically expensive (its specific exergy is assumed to be 2.5 MJ/kg methane), the separation of methane from the produced gas stream is not desirable. The highest exergy recovery factor is obtained for Scenario 1. Despite the large investment in CO_2 capture, transportation, and compression, injection of CO_2 leads to exergy gain because of high specific exergy of the crude oil. Fig. 12 shows that for the case considered here, the separation of methane from CO_2 accounts for more than 30% reduction in the exergy recovery factor (for the average mass
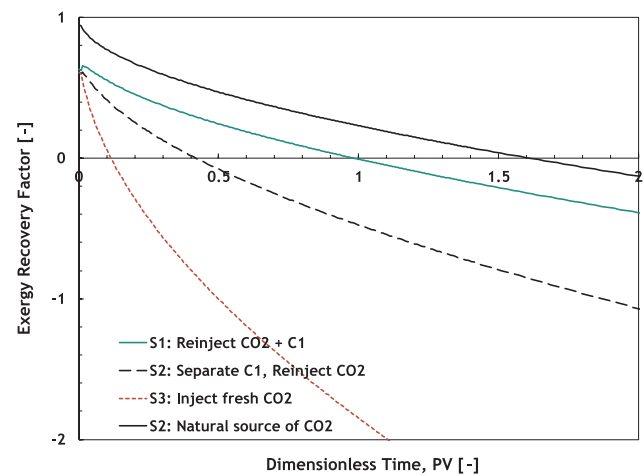

Fig. 11. Effect of gas separation on the exergy recovery factor calculated for Case 2 (medium heterogeneous case).
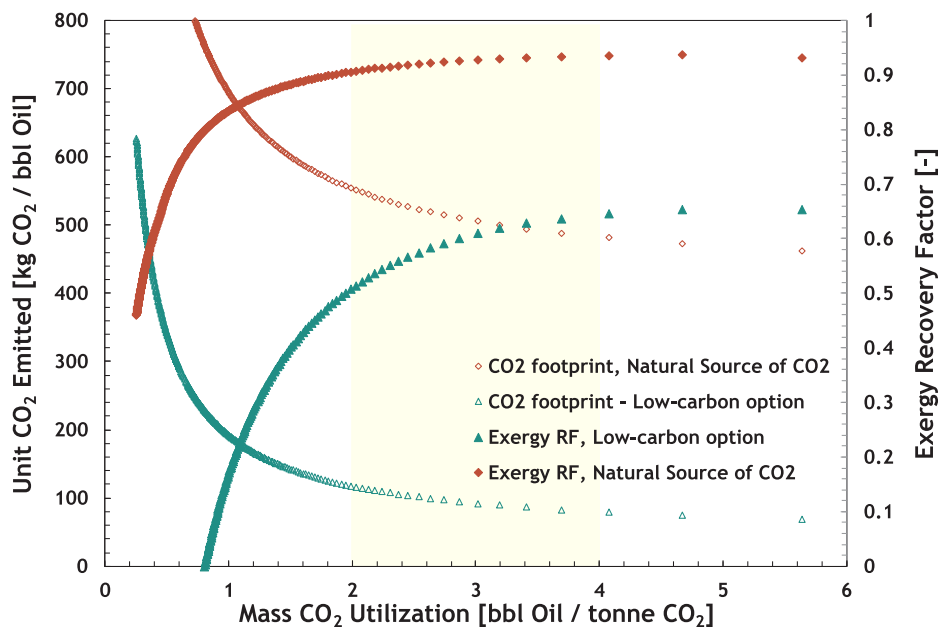

Fig. 10. Unit CO_2 emitted (kg CO_2/bbl oil) and exergy recovery factor as a function of gross mass CO_2 utilization factor for Scenario 1. The shaded area highlights the range of CO_2 emission and exergy recovery factor based on the utilization factor of the current CO_2-EOR projects. The figure includes CO_2 released from combustion of oil (~ 422 $kgCO_2$/bbl).
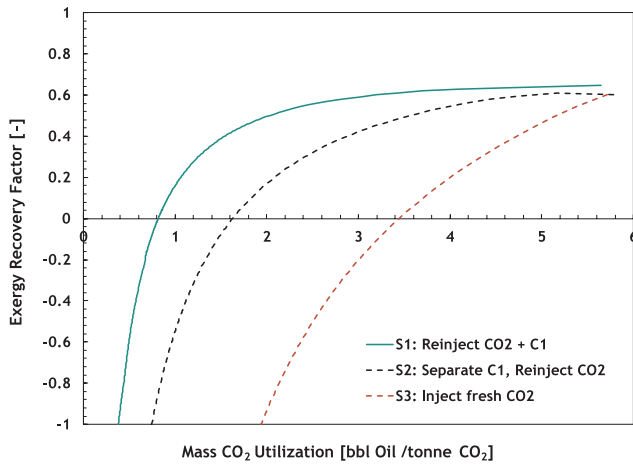
Fig. 12. Exergy recovery factor as a function of mass CO_2 utilization factor for Case 2 (medium heterogeneity) with the scenarios considered for the produced gas stream.

CO_2 utilization factor of 2 bbl/tCO_2). The difference between Scenarios 1 and 2 depends on the amount of dissolved gas in the oleic phase (or GOR) and lost (or retained) volume of the gas in the reservoir. The difference between the different scenarios decreases as the CO_2 utilization factor increases. This emphasizes the importance of finding ways (e.g., foam) to improve the CO_2 utilization factor.

The majority of the current CO_2-EOR projects uses relatively pure CO_2 extracted from natural sources (i.e. from underground formations) and therefore little exergy is consumed to provide CO_2. The solid black line in Fig. 11 depicts the effect of exergy of capture on the exergy outcome of the CO_2 EOR project for Scenario 2. The exergy recovery increases when this exergetic cost is omitted. CO_2-EOR using the natural sources, even if it leads to significant exergy gains, increases the CO_2 levels in the atmosphere, because it takes the already-stored CO_2 to the surface.

6. Concluding remarks

We perform an analysis to assess whether and under which circumstances it is exergetically efficient to store CO_2 through enhanced oil recovery (EOR). We use pilot examples of CO_2-EOR in combination with the modified Koval method to generate an estimate of the expected oil production history. The system considered includes CO_2 capture, initial compression at the capture site, transport to the oil field, re-compression in the oil field, water injection, separation of the gas stream, oil transport to the refinery, and oil and gas production from the reservoir. The following conclusions are drawn from this study:

- The life cycle of CO_2-EOR with the CCS option can be assessed with the exergy concept. Using the method developed and illustrated, the

carbon footprint of each stage of the process can also be quantified.
- The exergy recovery factor, the ratio between the produced exergy corrected for material and process exergy requirements for its extraction and the gross exergy of the source, decreases with time.
- For CCS to be an efficient way of reducing CO_2 concentration in the atmosphere (1) the exergetic cost of CO_2 separation should be reduced considerably, and/or (2) the source of energy should be a low carbon source. With the currently large exergetic cost of CO_2 separation, CCS is likely to return significant amounts of CO_2 to the atmosphere, regardless of the cost. Depending on the type of the power-plant fuel (gas, oil or coal), a minimum of 0.43–0.94 kg of CO_2 can be emitted per kg of CO_2 stored.
- The maximum net storage efficiency is 10–56% of the captured CO_2. Practically, with current state of technology, the CCS process using energy from coal-fired power plants will likely generate more CO_2 than stored.
- From thermodynamics point of view, CO_2 EOR with a CCS option is unsustainable, that is during the life cycle of the process more exergy is consumed than the exergy produced from oil.
- The exergy recovery factor of CO_2-EOR depends on the CO_2 utilization factor which, based on field experience, is currently in the range of 2–4 bbl-oil/tCO_2. For this CO_2 utilization range, 35–50% of the exergy produced from oil should be invested to capture, transport, and use CO_2 as an EOR agent.
- The utilization of CO_2 captured from power plants for EOR leads to 30–40% less exergy extraction compared to the case with natural source of CO_2; however, this leads to storage of more than 400 kg of extra carbon dioxide per barrel of oil produced.
- Combination of CCS with EOR reduces the full-cycle unit CO_2 emission to less than 100 kgCO_2/bbl.
- The highest exergy recovery factor (or lowest CO_2 emission) is obtained when produced gas stream is reinjected to reservoir without separation.
- Improvements of the CO_2 utilization factor (by implementing conformance/mobility control techniques) are required to reduce the CO_2 footprint of the CO_2-EOR projects.

CRediT authorship contribution statement

R. Farajzadeh: Conceptualization, Formal analysis, Methology, Supervision, Writing - original draft. **A.A. Eftekhari:** Software, Writing - review & editing. **G. Dafnomilis:** Formal analysis. **L.W. Lake:** Writing - review & editing. **J. Bruining:** Writing - review & editing, Supervision.

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Appendix A

A.1. Exergy analysis: General concept

The exergy of a substance is a function of its temperature, pressure and composition, as well as of the average temperature, pressure and composition of its surrounding environment (also known as the dead state) [34,35]. Exergy can also be a function of location (potential exergy) and velocity (kinetic exergy). These functionalities are defined later in this section. The exergy of a system in equilibrium with the environment is zero. For practical reasons, we take the dead state to be at $T_0 = 298.15$ K and $P_0 = 1$ bar. In the following we denote the exergy by Ex [J] and its rate by $\dot{Ex}$ [J/s]. The specific exergy is then defined by $\dot{ex} = \dot{Ex}/\dot{m}$ [J/kg], where $\dot{m}$ [kg/s] is the mass flow rate of the material stream.

Exergy transfer rate associated with the material streams is given by

$$\dot{Ex} = \dot{Ex}^{ke} + \dot{Ex}^{p} + \dot{Ex}^{ph} + \dot{Ex}^{ch} \tag{A.1}$$

where $\dot{Ex}^{ke} = \frac{\dot{m}V_0^2}{2}$ is the kinetic exergy rate (V_0 is the speed of the stream, with flow Q [m^3/s] relative to the earth surface), $\dot{Ex}^{p} = \dot{m}gZ_0$ is the

potential exergy rate (where g is the acceleration due to gravity and Z_0 [m] is the stream altitude above sea level), $\dot{E}x^{ph}$ [J/s] represents the physical or thermo- mechanical exergy based on the temperature and the pressure difference between the stream and the dead state, and $\dot{E}x^{ch}$ [J/s] is the chemical exergy based on the difference between the chemical potentials of the components in the stream and the dead state.

The thermo-mechanical or the physical exergy is the work that can be obtained by taking the substance through a reversible process from its initial state (T,P) to the state of the environment (T_0,P_0). The specific physical exergy is written as

$$ex^{ph} = h - h_0 - T_0(s - s_0) \tag{A.2}$$

For an ideal gas with a constant heat capacity C_p [J/(mol K)] Eq. (A.2) becomes

$$ex_{gas}^{ph} = C_p T_0 \left(\frac{T}{T_0} - 1 - \ln \frac{T}{T_0} \right) + RT_0 \frac{P}{P_0} \tag{A.3}$$

For solids and liquids assuming a constant heat capacity c [J/(mol K)] the physical exergy can be calculated from

$$ex_{ls}^{ph} = c \left[(T - T_0) - T_0 \ln \frac{T}{T_0} \right] - \upsilon_m (P - P_0) \tag{A.4}$$

where υ_m [m³/mol] is the molar volume of the substance at temperature T_0.

The specific chemical exergy at T_0 and P_0 can be calculated by bringing the mixture component into chemical equilibrium with the environment. In practice, it is more convenient to use the chemical exergy of the elements to calculate the chemical exergy of pure components. Using the standard chemical exergies of the elements, the standard chemical exergy of compounds can be calculated from [34,35]

$$\dot{E}x^{ch,0} = \Delta_f G^0 + \sum_{el} n_{el} \dot{E}x_{el}^{ch,0} \tag{A.5}$$

where $\Delta_f G^0$ [J] is the standard Gibbs energy of formation of the compound, n_{el} is the number of moles of the element per unit of the compound, and $\dot{E}x_{el}^{ch,0}$ [J/mol] is the standard chemical exergy of the element. The chemical exergy of a mixture with composition x_i is then calculated by

$$\dot{E}x^{ch} = \Delta_{mix}H + \sum_i x_i \dot{E}x_i^{ch,0} \tag{A.6}$$

where $\Delta_{mix}H$ is the enthalpy of mixing.

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